The Reliability of the Reversible Hydrogen Electrode (RHE): From Theory to Experiment

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The recent times are marked by the massive amount of new electrocatalysts being developed to interest reactions such as water splitting, CO_2 reduction and ammonia generation. The reversible hydrogen electrode (RHE) enters as an often choice to conversion from different reference electrodes commonly employed in these catalytical assays and thus compare the results. The main reason lies in the dependence on the pH to the potential values which in theory the values can be converted according to the acidity of the media whether buffered or not.[1] With effect most papers dealing with the use of RHE do it only theoretically as it is very sensible to the reference surface pH. Also, the expression from conversion potentials comes directly from the Nernst equation, which does not take into the account the non-stoichiometry ratio between acid and hydrogen (2:1).[2] Under the light of this subtleties we tried to put the RHE up to test and to exert a better correlation between RHE and the other common electrodes We investigated the hydrogen redox pair in Pt electrodes as empirical model to the RHE by performing cyclic voltammetry (CV) experiments in strong and weak acidic media. By evaluating the midway potential (E_{mid}) from the CV, together with the limiting flux (j_{lim}) of the electrode we were able to extract a better equation to the RHE considering the effects of the flux on this non-stoichiometric reaction in different media. Also, the hydrogen redox pair were simulated in the presence of both weak and strong acids using a finite numerical differentiation (FND) script on Python. Whit both empirical analysis and simulation we were able to validate the analytical expression obtained from the theory.

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References:

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